Photodegradation of herbicide triasulfuron

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Abstract: Triasulfuron was degraded in aqueous solution by ultraviolet irradiation to yield 2-chloroethoxybenzene and (4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea. The reaction followed first-order kinetics. In sunlight, the reaction was slower and afforded these two photoproducts together with 2-amino-4-methoxy-6-methyltriazine and 2-(2-chloroethoxy)benzenesulfonamide. The latter compounds arise from hydrolytic cleavage of the sulfonylurea bridge of triasulfuron because of the acidity of the reaction medium due to the loss of sulfur dioxide. A mechanism which accounts for the formation of the photoproducts is proposed.

Keywords: triasulfuron; sulfonylureas; photolysis; phototransformation

1 INTRODUCTION

Triasulfuron is a selective sulfonylurea herbicide used at very low rates (10–25 g ha^{-1}) for weed control in cereals.[1] Sulfonylurea herbicides are degraded in soil by chemical hydrolysis and microbial activity.[2] Generally, the hydrolysis involves the breakdown of the sulfonylurea bridge to give the corresponding sulfonamide and a heterocyclic amine. Photolysis is considered as only a minor degradation process for sulfonylureas. Nevertheless, for this class of herbicide, several reports indicate that photodegradation is an alternative pathway to chemical hydrolysis.[3–5] Previous studies of ours showed that triasulfuron is more persistent in neutral or weakly basic than in acidic solution.[6] The hydrolysis reaction is first-order and pH-dependent, yielding at least five metabolites. At all pH values studied, the primary pathway of degradation involves the cleavage of the sulfonylurea bridge. Minor degradation mechanisms were observed, such as *O*-demethylation and opening of the triazine ring. However, no studies concerning the photodegradation of triasulfuron are available. This paper reports the photochemical degradation of triasulfuron and the nature of degradation products. Based on the results, a degradation pathway is proposed.

2 MATERIALS AND METHODS

2.1 Chemicals

Triasulfuron (1; purity 99.5%) was supplied by Ciba-Geigy, Saronno, Italy. Its purity was checked by HPLC. 2-Chloroethoxybenzene (or *β*-chlorophenetole) (2) was supplied by Aldrich (Milan, Italy). 2-Amino-4-methoxy-6-methyltriazine (4), 2-(2-chloroethoxy)benzenesulfonamide (5) were obtained according to a published procedure.[6]

2.2 Photochemical procedure

The UV spectrum of triasulfuron is characterised by an intense absorption at 224 nm and a weak band at 280 nm (Fig 1). The absorption is very weak at wavelengths longer than 300 nm. Since triasulfuron is scarcely soluble in water, a stock solution containing 3.1 mmol litre^{-1} (1.25 g litre^{-1}) of herbicide in acetonitrile was prepared. The solution, maintained in the dark at 5°C, was stable for a prolonged time. In the photolysis experiments, aliquots of the stock solution (1 ml) were diluted to 100 ml with acetonitrile + water (49 + 51 by volume). The final concentration of triasulfuron in the test solutions was 31 μM.

Solutions contained in a water-cooled quartz flask were irradiated in a merry-go-round Rayonet photoreactor with low-pressure mercury lamps emitting at 254 nm. For irradiation at 300 and 366 nm, fluorescent lamps and black light fluorescent lamps, respectively, were used. A water-cooled borosilicate flask was used for irradiation at 366 nm.

Dark control experiments were carried out in conditions similar to those described above, except that the photoreaction vessel was covered with aluminium foil.

At appropriate times, depending on the photolysis rate, each test solution was analysed directed by HPLC. All the experiments were run in triplicate.

2.3 Photoproducts

Samples (50 ml) of the stock solution, after dilution with distilled water (50 ml), were irradiated at

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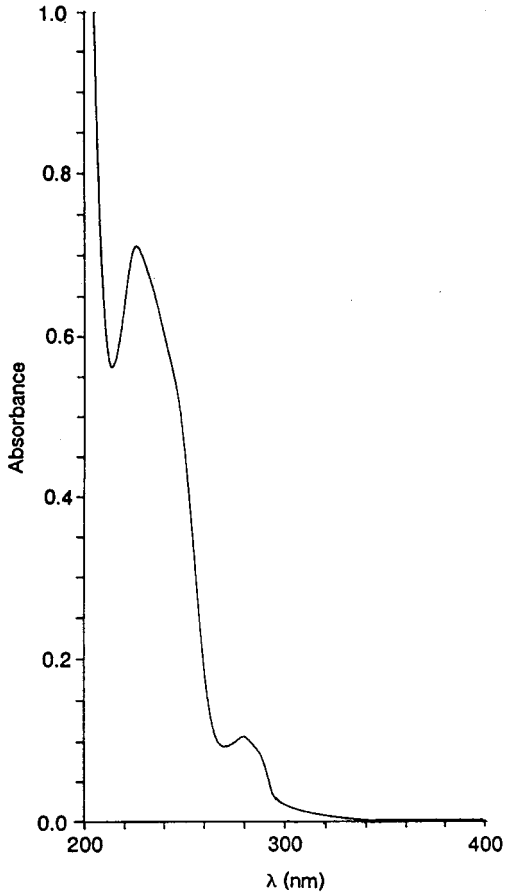

Figure 1. UV spectrum of triasulfuron in acetonitrile + water (50 + 50 by volume).

254 nm for 10 min. The crude reaction mixture was concentrated under vacuum at room temperature. Photoproducts were isolated by column chromatography on Merck silica gel (Kieselgel 40, 70–230 mesh) using ethyl acetate as eluant. The products obtained after the clean-up procedure were the same as in the crude reaction mixture. The run was repeated three times in order to obtain sufficient photoproduct for analytical measurements.

2.4 Analytical methods

The decrease of triasulfuron during the photolysis was estimated by HPLC. A Waters 510 liquid chromatograph equipped with a Spherisorb C_8 analytical column (5 µm, 4.6 × 250 mm), a multiwavelength Waters 490 programmable detector operating at 224 nm and a Waters Baseline 810 chromatography work-station, was used. The mobile phase was acetonitrile + water (40 + 60 by volume) previously brought to pH 2.7 with phosphoric acid. The flux rate was 1 ml min^{-1}. The retention times for triasulfuron and its metabolites, under the chromatographic conditions described, were 8.7, 19.9 and 1.9 min for the compounds **1**, **2** and **3**, respectively.

NMR (nuclear magnetic resonance) spectra were determined on a Bruker AC-P (300 MHz) NMR spectrometer using Bruker software.

Mass spectra were obtained on a Perkin Elmer SCIEX API III-Plus (atmospheric pressure ionisation) spectrometer equipped with an ion spray liquid-mass interface.

3 RESULTS AND DISCUSSION

3.1 Photolysis at 254 and 300 nm

The linearity of the plot of the concentrations of **1** (ln values) *versus* time (Table 1), for the irradiation at 254 nm, suggests that the photolysis follows pseudo-first-order kinetics. The degradation of triasulfuron yielded equimolar amounts of 2-chloroethoxybenzene (2) and a monosubstituted urea (3) (Fig 2). The two photoproducts were isolated by chromatography. Metabolite **3** was obtained as white crystals: MS (*m*/e): 184 $(MH)^+$, 141 (184-HNCO). Its structure was confirmed by [^{1}H] and [^{13}C] NMR (Table 2). The identity of photoproduct **2** was checked by comparison of its spectral and chromatographic features with those of an analytical standard.

The mechanism leading to these products can be interpreted according to the scheme shown in Fig 2. The formation of **2** by irradiation of triasulfuron supports a homolytic carbon–sulfur cleavage. This fragmentation is followed by the loss of sulfur dioxide to produce the amine radical. Sulfur dioxide increases the acidity of reaction medium. The subsequent H-abstraction from water affords products **2** and **3**. In fact, in plain acetonitrile, which is an inef-

Table 1. Rate constants (k) and half-life ($t_{1/2}$) values for triasulfuron photodegradation at different wavelengths

λ(nm)	k	$t_{1/2}$	r^2
254	0.349 min^{-1}	2.0 min	0.995
300	0.005 min^{-1}	13.5 min	0.998
366	0.071 d^{-1}	9.7 days	0.991

Table 2. [^{1}H] and [^{13}C] NMR chemical shifts for photoproducts 3[a]

[^1H] NMR		[^{13}C] NMR	
Assignment	$\delta_{H\ (ppm)}$	*Assignment*	$\delta_{(ppm)}$
			177.91
CONH	9.87 (1H, s)	triazine ring	170.11
			164.54
	8.24 (1H, s)		
$CONH_2$		C=O	153.68
	7.24 (1H, s)		
OCH_3	3.92 (3H, s)	OCH_3	54.58
CH_3	2.40 (3H, s)	CH_3	25.03

[a] DMSO-d_6. T = 308 K

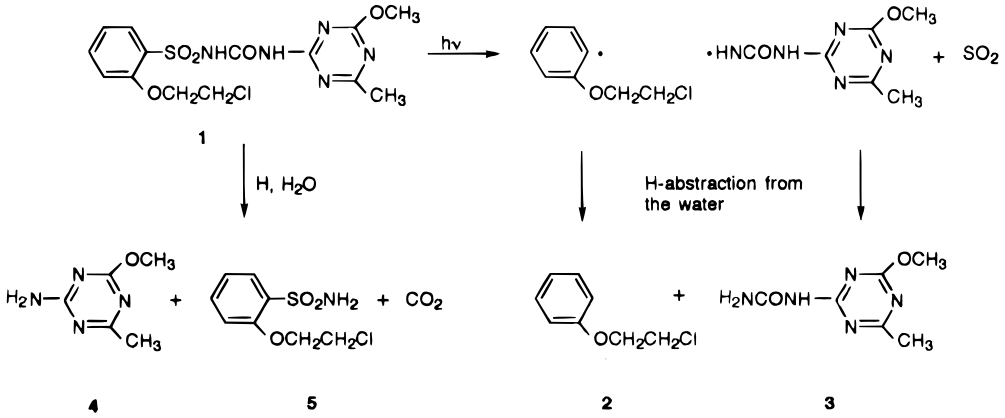

Figure 2. Proposed mechanism for the photodegradation of triasulfuron.

ficient hydrogen donor, photochemical decomposition of **1** did not occur.

This mechanism is analogous to that occurring in the photochemical deprotection of amino groups by a photoremovable group as sulfonamide.[7–9] Sulfonamides are among the most effective groups in protecting amino functions. Their effectiveness arises from their stability in the presence of dilute acids and bases, combined with their facile removal by photolysis. The analogous compound of photoproduct **3** was observed by Choudhury and Dureja[4,5] during the photolysis of chlorimuron-ethyl both in water and on soil.

The photolysis of triasulfuron at 300 nm followed pseudo-first-order kinetics (Table 1). The reaction was slower because of the low absorptivity of herbicide in the UV region at this wavelength value. The photodegradation yielded equimolar amounts of **2** and **3** as the only products.

3.2 Photolysis at 366 nm

No reaction occurred in simulated sunlight conditions and triasulfuron was recovered almost unchanged after 24 h irradiation.

After prolonged irradiation times, triasulfuron decomposes with pseudo-first-order kinetics (Table 1). After 9 days irradiation, the crude reaction mixture exhibited the following product distribution percentages: **1**, 49%; **2**, 15%; **3**, 15%; 2-amino-4-methoxy-6-methyltriazine (**4**), 10%; and 2-(2-chloroethoxy)benzenesulfonamide (**5**), 10%; see Fig 2. The last two compounds, most probably, do not form directly by a photochemical mechanism. It is likely that the acidification of reaction medium produced by the loss of sulfur dioxide and the prolonged reaction time favour a heterolytic hydrolysis. Accordingly, the irradiation of triasulfuron, at 366 nm, in buffered solution at pH 7 afforded only compounds **2** and **3**. These findings are in agreement with the results obtained by Braschi *et al*,[6] who reported that compounds **4** and **5**, arising from the hydrolytic cleavage of the sulfonylurea bridge of triasulfuron, are the main metabolites in the pH range 2–5.

3.3 Concluding remarks

In conclusion, this study provides basic information about the photoreactivity and the photoproducts of triasulfuron. Under simulated sunlight condition the herbicide degrades slowly, but much faster than via chemical hydrolysis (in buffered aqueous medium at pH 7, $t_{1/2} = 492$ days).[6] Therefore, photolysis, in combination with chemical and microbial degradation, could contribute to the detoxification of triasulfuron in aquatic environments.

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